NATIONAL BUREAU OF STANDARDS REPORT

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Progress Report

on

DENTAL CEMENTS, DIRECT FILLING RESINS, COMPOSITE
AND ADHESIVE RESTORATIVE MATERIALS: A RESUME

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U.S. DEPARTMENT OF COMMERCE
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DENTAL CEMENTS, DIRECT FILLING RESINS, COMPOSITE AND ADHESIVE RESTORATIVE MATERIALS: A RESUME

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Dental Cements, Direct Filling Resins,
Composite and Adhesive Restorative Materials: A Resumé *

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Dental Cements, Direct Filling Resins,
Composite and Adhesive Restorative Materials: A Resume

Synopsis: This resume concerns: (1) experimental and
commercial dental cements and restorative and adhesive
materials usually containing nonmetallic inorganic
components; (2) the biocompatibility of (1) with
oral tissues; (3) proposed methods of bioevaluation;
(4) the oral environment; (5) the nature of the hard
tooth tissue; (6) cavity treatment; (7) agents for
bonding the restorative material to the tooth; and
(8) 112 references.

The cements include those based on: (C-1) zinc
oxide-eugenol with additives such as zinc acetate,
rosin, polymers and most important o-ethoxybenzoic
acid (EBA); (C-2) metallic oxides-phosphoric acid;
(C-3) acid phosphate salts-water; (C-4) aluminosilicate
glass-phosphoric acid; (C-5) zinc oxide-polyacrylic acid;
(C-6) methyl methacrylate-poly(methyl methacrylate) with
or without inorganic fillers. Direct filling resins
(C-6) without filler and composite restorative materials
(C-6) with filler are based on acrylic resins or reaction

products of acrylic (methacrylates) with other resins.
Coupling agents include cyanoacrylates, epoxy-acrylic
adducts and polyurethanes. The 10 tables give com-
position, values for pertinent physical properties or
dental requirements. (C-2) dominates the cements but
(C-1) with (EBA) and (C-5) which has some adhesion
to hard tooth tissues and stainless steel may displace
(C-2). (C-4) restorative materials are anticariogenic
and widely used but are being supplanted by composite
restorative materials.

Cements

Cements developed for special purposes are extensively used in dentistry as filling materials, luting media, obtundent dressings, impression pastes and as a base for other restorative materials.

Current dental cements usually consist of a powder or paste that is mixed with a paste or liquid. The resultant mixture passes through a plastic manipulative state, which is probably colloidal, and has a continuing increase in viscosity until it finally solidifies.

Currently used cements include: (1) zinc oxide-eugenol and modifications thereof; (2) phosphoric acid liquid mixed with a variety of metal oxides or mixtures of them including zinc oxide, magnesium oxide, cupric oxide, cuprous oxide, manganese oxide, and/or with a complex, alkaline, alumino-silicate glass, or acid phosphate salts mixed with water; (3) resin cements based on acrylic monomers and polymers; and (4) a new cement with a modified zinc oxide powder and a polyacrylic acid liquid.

Zinc oxide-eugenol cement (ZOE). About a century ago one of the currently used cements consisting of powdered zinc

oxide mixed with eugenol was used in dentistry. The set cement is a complex solid consisting of particles of zinc oxide bound together by zinc eugenolate and of eugenol which is sorbed by both the zinc oxide and the zinc eugenolate.[1] The hardening time of an unmodified zinc oxide-eugenol cement is very long, usually several days, if moisture is absent.

Perhaps the first important additive was small amounts of zinc acetate which accelerated the reaction. Later, hydrogenated rosin was added to increase strength and decrease brittleness. Polystyrene and poly(methyl methacrylate) have a similar effect. Because of low strength, poor abrasion resistance and disintegration in the mouth, a search was made for other metal oxides and chelating agents that would improve the values for the foregoing pertinent physical properties. One of these investigations recommended a solution of eugenol and o-ethoxybenzoic acid (EBA), which when mixed with powdered zinc oxide, had a short setting time and a marked increase in compressive strength and, unfortunately, in water solubility.[2] Powdered quartz[2] and alumina[3] additions further enhanced the quality.

A comprehensive review of zinc oxide-eugenol type cements with an extensive bibliography is available.[2].

There are now commercially available modified zinc oxide-eugenol cements with characteristics which some users believe are suitable for permanent cementation of restorations in the mouth, but until solid clinical evidence is available, caution is advised because of their water solubility. These cements have obtundent properties and have little or no irritating effect on the pulp. The biologic acceptance of zinc oxide-eugenol based cements is the best available and has become almost a standard for comparing the effects of other cements.

Table 1 shows the composition and proportions of powder and liquid with values for a few pertinent physical properties of certain zinc oxide and eugenol-based cements. The table cannot be used for direct comparisons of the effect of additives because of the many variables not only in the substances used in compounding the cements but also in the test procedures, especially the proportions of powder and liquid. The table does give some idea of the range of highest values for compressive strength encountered in

Table 1

Zinc Oxide-Eugenol Based Cements: Composition and Properties

| Composition in weight percent | | Powder-liquid proportions | Time of setting | Solubility and disintegration after 7 days | Compressive strength at 7 days * |
Powder	Liquid	Grams of powder in 0.4 ml of liquid (6)	Minutes (6)	% by weight (6)	kgf/cm² (6)
Zinc oxide 99.8 Zinc acetate 0.2 (5)	Eugenol 100 (5)	2.2	5.5	0.1	140
Zinc oxide 70.25 Hydrogenated rosin 29.40 Zinc acetate 0.35 (5)	Eugenol 85 Olive oil 15 (5)	8.5	9.0	0.02	390
Zinc oxide 68.8 Silica 30.6 Zinc acetate 0.6 (2)	O-ethoxybenzoic acid 75 Eugenol 25	3.25	8.0	3.2	820
Zinc oxide 89.7 Silica 10.0 Zinc acetate 0.3 (7)	O-ethoxybenzoic acid 47.5 Eugenol 47.5 Poly(methyl-methacrylate) 5.0	Variable	4	2.68	510
Zinc oxide 64 Alumina 30 Hydrogenated rosin 6	O-ethoxybenzoic acid 62.5 Eugenol 37.5	4.2	8.5	0.03	1060
Six available commercial cements (8)		Variable	7-20	---	24 hour 6-220

* 1 kgf/cm² = 14.223 psi

existing and experimental cements having a zinc oxide-
eugenol base. Most of the values were obtained by test
methods, or variations thereof, given in American Dental
Association Specification No. 8 for Dental Zinc Phosphate
Cement.[9]

Current research is centered on developing high-
strength, low-solubility cements with good bioacceptance
not only for temporary filling materials, but more
importantly, for cementing media.

Zinc Phosphate Cements. Dental cements based upon a phos-
phoric acid liquid have been used in dentistry for at
least a century and a half. The most important one is
zinc phosphate cement in which powdered sintered zinc
oxide and magnesium oxide (usually 9:1 ratio) is mixed
with a phosphoric acid solution buffered by aluminum or
zinc salts and sometimes by both. These cements are often
improperly referred to as oxyphosphate of zinc cements but
they contain no oxy-salts.

The set cement consists of unreacted cores of powder
particles bound together with a matrix of the phosphates of

zinc, magnesium and aluminum. Prior to this hardened
state the mixed but not completely set cement is in a
plastic doughy state which some investigators believe
is colloidal.

Crowell[10] showed that $ZnHPO_4 \cdot 3H_2O$ was the
principal crystalline phase in the set cement and that the
desirable plasticity of mixed but unset cement was caused
by $ZnHPO_4 \cdot 3H_2O$ being formed in the cement liquid during
mixing.

The requirements of the first revision (1938-1967)[11]
and the current revision (1968)[9] of A.D.A.Specification
No. 8 for Dental Zinc Phosphate Cement and properties of
dental zinc phosphate cements[12] on the List of Certified
Dental Materials as established by the American Dental
Association[13] and some later values are given in Table 2.

Although there have not been any significant improve-
ments in zinc phosphate cements since early in this century,
nothing has been able to displace their use because nothing
better has been developed for a sufficient time to determine
the long-time clinical behavior. It may be that the improved

zinc oxide-eugenol or the new zinc oxide-polyacrylic acid type cements will displace zinc phosphate cements but it takes time to displace old materials unless there are gross and dramatic improvements in clinical performance in the new ones.

In Japan water-settable zinc phosphate cements were developed in which the powder contained not only zinc oxide but also phosphate salts, some of which were acidic. The liquid was water.[17] The powder of one consisted of zinc oxide, monozinc phosphate and tertiary zinc phosphate[18] while others contained monocalcium and monomanganese phosphates.[16,19]

The properties of these "water-settable" zinc phosphates have been determined by several investigators. Data from two[15,16] are given in Table 2.

The water-settable phosphate cements cannot compete with the customary zinc phosphate cements because the acid phosphate salts are too hygroscopic resulting in poor keeping qualities.

Table 2

Zinc Phosphate Cements: Composition and Properties
Zinc Phosphate Cements

	Arsenic Content	Consistency of Mix	Time of setting		Maximum film thickness		Compressive strength (minimum – 24 hours)†	Solubility and disintegration (maximum – 24 hours)
Requirements of revised ADA Specification No. 8 for Dental Zinc Phosphate Cements (1968–)* (9)	Maximum percentage by weight	Grams of powder in 0.5 ml of liquid to produce a disk 30 ± 1 mm in diameter	Min. minutes	Max. minutes	Type 1	Type 2	kgf/cm²	% by weight
	0.0002		5	9	μm 25	μm 40	700	0.2
Requirements of former ADA Specification No. 8 for Dental Zinc Phosphate Cement (1938-1967) (11)	0.0002	Same	4	10	40		(Minimum – 7 days) 840	(Maximum – 7 days) 0.30
Range of values for zinc phosphate cements on List of Certified Dental Materials (1958) (12,13)	<0.0002	1.3 ± 0.3 (1.2 ± 0.1)**	7 ± 1 (8 ± 1)**		30 ± 10 (25)**	** (28±2)	1180 ± 280 (840 ± 50)**	0.1 ± 0.1 (0.1 ± 0.0)**
Composition Percentage by weight (14) Powder: ZnO 89.5 MgO 9.4 BaCrO₄ 0.8 Liquid: PO₄ 57.9 Al 2.8 Mg 0.3		Disk was 34 ± 1 mm in diameter 1.00	9		17		950	0.14

Water-settable zinc phosphate cement

New Calmix (Sankin Chemical Industry Co., Ltd. (Tokyo, Japan) (15)	1.6		8½		75		670	0.4
Powder (16) Monomanganese phosphate (coated with zinc hydroxide) Zinc oxide	Liquid Water	---	5⅓		31		850	0.36
Zinc oxide Monomanganese phosphate dehydrated 240°C for 50 minutes	Water	---	6⅓		27½		1250	0.34
Zinc oxide Monomanganese phosphate dehydrated 250°C for 50 minutes Tertiary zinc phosphate	Water	---	6½		28		1100	0.08

*   The same as Federation Dentaire Internationale (FDI) Specification No. 6 for Dental Zinc Phosphate Cement. Internat. Dent. J. 13:138 March 1963 and International Organization for Standardization (ISO) Draft ISO Recommendation No. 1566. Dental Zinc Phosphate Cement.

**   Range of unreported values for six zinc phosphate cements currently in use. Data from American Dental Association Council on Dental Materials and Devices, Chicago, Ill.

†   1 kgf/cm² = 14.223 psi.

Copper Phosphate Cements. The copper phosphate cements are being used less and less because they irritate the pulp tissue more than the zinc phosphate and zinc oxide-eugenol cements. In addition, the black copper cement is many times more soluble in water than is zinc phosphate cement.

Data from the most extensive investigation[20] of the properties of these cements are given in Table 3. The values were derived by the methods described in the A.D.A. Specification No. 8 for Dental Zinc Phosphate Cement-- First Revision (1938).[21]

Zinc Polyacrylate Cements. An entirely new cement[23] is being found useful. It is appropriately called zinc poly- acrylate cement but has been called zinc carboxylate cement. It is made by adding zinc oxide to an aqueous solution of polyacrylic acid using the conventional hand mixing method. One of the special features of the experimental cement is its ability to adhere to tooth enamel and dentin[23] (Table 4) and to stainless steel.[25]

The cement is patented through the National Research and Development Corporation in the United Kingdom.[23] Two commercial products are available (March 1970)--Durelon,

Table 3

Copper Phosphate Cements: Composition and Properties (24)

Composition of powder percent by weight	Grams of powder in 0.5 ml of liquid to produce a disk 30 ± 1 mm in diameter*	Time of setting	Film Thickness	Compressive strength at 7 days ††	Solubility and Disintegration at 7 days
		minutes	μm	kgf/cm²	% by weight
Ames Copper Cement (20) CuO 91.5 Co₃O₄ 8.4 ---	2.2†	5	50	1550	2.7
Fleck's Red Copper Cement (20) Cu₂O 23.9 ZnO 66.7 ---	1.5	5 - 5½	25 - 30	1040	0.5
Ames Copper Cement (6)	Grams of powder in 0.4 ml of liquid to produce a disk 25 ± 1 mm in diameter** 5.5	5.5	---	630	3.7
Fleck's Red Copper Cement (6)	3.5	3.5	---	1480	0.05

* Cementing consistency--ADA Specification No. 8 for Dental Zinc Phosphate Cement(21)

** Filling consistency--ADA Specification No. 9 for Dental Silicate Cement(22)

† Recommended by manufacturer

†† 1 kgf/cm² = 14.223 psi

Table 4
Zinc Polyacrylate Cements
(Liquid-aqueous solution of polycarboxylate acid. Powder essentially zinc oxide

Material	Powder/Liquid Ratio	Adhesive strength		Compressive strength *	Tensile strength (diametral)*	Water uptake	Dimensional change (linear)	Solubility
		Enamel*	Dentin*					
Experimental (23) Lining 1		kgf/cm² (A) 150	kgf/cm² (A) 50	kgf/cm² 1200	kgf/cm² 140	% by weight	%	% by weight
Lining 2	2:1			910	105	-		
Cementing				670	64			
Experimental (26) Cementing	2:1	85	·					
		78-87						
		57						
		45						
	3:1	79						
Poly-C (24) Lining	(by weight) 1:50	(D) (B) (C)		(M) 460	(G) (L) 56-79	(D) 3.0) (R)	(D) (J) + 0.8	
Lining	1:43	0 to 22		537 (N) (O)	(H)			0.8 (V)
Cementing	1:92			372 (P)	32-34	2.3 (D) (S)	+ 0.5 (D) (J)	0.4 (V)
Cementing	1:38			452 (P)				
Durelon	1:4 to 1:6	11 to 98 (B) (C)(D) 0 to 61 (E)		(K) 143 - 499	(F) 46-64	(D) (Q) 5.2 - 7.2	(D) (J) + 4.2	
Durelon** (24)						1.3 - 1.4 (D) (U)		0.6 (V)
DeTrey's (24) Zinc Phosphate Cement	2:5 to 3:48		(B) 0 (D)	702-1075	(I) 54-62	(T) 0.9		(V) 0.3

* 1 kgf/cm² = 14.223 psi

** Samples obtained from manufacturer's improved batches.

(A) Values converted from lb/in³ to kgf/cm² and rounded off.
(B) If the assembly fell apart in handling a zero value is given.
(C) Teeth stored in 70% alcohol for some months before being used.
(D) Powder/liquid ratio not given.
(E) Teeth were freshly extracted (1-3 days).
(F) Powder/liquid ratio 1.5:1
(G) Powder/liquid ratio 1.6:1.
(H) Powder/liquid ratio 1.9:1.
(I) Powder/liquid ratio 3:1 - Specimens 3 to 64 hours old.
(J) Calculated from author's data. Specimens were 3 weeks in water.
(K) When Durelon was immersed in water for 28 days, the compressive strength
     decreased from 450 to 162 kgf/cm².
(L) Specimens 20 hours old.
(M) Specimens 4 hours old.
(N) Specimen 64 hours old.
(O) When cement specimens were stored in water for 28 days compressive
     strength was 380 kgf/cm³. Powder/liquid ratio was not given.
(P) When cement specimens were stored in water for 28 days, compressive
     strength was 470 kgf/cm³. Powder/liquid ratio not given.
(Q) Specimens immersed in water from 180 to 288 hours. At 2000 hours the
     value was about 12 per cent and equilibrium had not been established.
(R) Specimens immersed in water for 117 hours. At 2000 hours the value
     was about 6.5% with equilibrium having been established after about
     250 hours of immersion.
(S) Specimens immersed in water for 166 hours. At 2000 hours the value
     was about 4.5% with apparent equilibrium having been established
     after about 250 hours of immersion.
(T) Specimens immersed in water for 800 hours with apparent equilibrium
     having been established after about 400 hours of immersion.
(U) Specimens immersed in water for 163-164 hours. At 400 hours the value
     was about 2%. Equilibrium was not established. Projection of the curve
     of water uptake with time would give values for about 2.5% at 600 hours
     and about 3.8% at 1000 hours.
(V) Solubility at 600 hours in water.

made by Espe, GmbH, Seefeld/Oberbay, Germany (USA distributor,

Premier Dental Products, Philadelphia, Pa. 19107) and de-

Trey's Poly-C, made by Amalgamated Dental Co., Ltd., of

the United Kingdom (USA distributor, Cladius Ash, Inc.,

655-73rd Street, Niagara Falls, N. Y. 14304). In the adver-

tisements for deTrey's Poly-C no mention is made of adhesion

to the hard tooth tissues or to stainless steel. However,

the Durelon advertisement states "long-lasting adhesion to

tooth structure". Two investigators[24] determined the

degree of adhesion and gave values for other properties of

the two foregoing trade brands of zinc polyacrylate cements

and of a zinc phosphate cement (deTrey's). They gave values

of adhesion from 0 to as high as 98 kgf/cm^2 (0-1390 psi).

The scatter of values in most types of adhesion tests is

very great and these are no exception. Then, too, different

types of tests for adhesion may give radically different

values.

Naturally, if one had a material which was adhesive to

both tooth enamel and to stainless steel one would immediately

think of attaching orthodontic devices directly to the tooth

without the customary banding. Two authors in a series
of investigations[25,27] have explored this technic. In
the first article[25] circular stainless steel orthodontic
buttons were cemented to polished enamel surfaces using
polycarboxylate cement, silico-phosphate cement, zinc
phosphate cement and copper phosphate cement and subjected
to tension after storage for 48 hours in water at 37°C. The
tensile strength bond values were 74 kgf/cm^2 (1050 psi),
27 kgf/cm^2 (380 psi), 4.6 kgf/cm^2 (65 psi) and 23 kgf/cm^2
(330 psi), respectively. Further investigation[26] showed
that the tensile bond strength of several experimental
polyacrylate cements were several times the magnitude of
those of other dental cementing media. Most of the failures
of the zinc polyacrylate cements occurred within the cement
and not at the cement-enamel interface.

After investigating[27] the reaction of the bond to
shear stress, to peel strength tests, to static and dynamic
fatigue tests, to thermal cycling, to surface roughness
variation and to contaminations likely to occur in the
mouth, the authors believed that limited
clinical trials are warranted in which the orthodontic
appliance parts are attached directly to the surfaces of
the teeth.

Smith, the inventor of the zinc polyacrylate cements,[23] is continuing his experimentation (at the University of Toronto)[28] by mixing other oxides with zinc oxide, with and without sintering, and by using liquids containing poly-acrylic acid of molecular weights from 5000 to 300,000. Some of the combinations with powder-liquid ratios from 1.5 to 2.5 gave compressive strength from 631 to 914 kgf/cm^2 (9,000-13,000 psi) and tensile strengths from 56 to 106 kgf/cm^2 (800-1,500 psi). The solubility in water was less than 0.03%. This low water solubility value may have been derived by using the test for solubility and disintegration in A.D.A. Specification No. 8 for Dental Zinc Phosphate Cement.[9] The solubility in water using other test methods is apparently much higher[24] (Table 4). In fact, the high water sorption, which caused dramatic decreases in strength and stiffness and increases in dimensions,[24] is a very important factor when considering the use of polyacrylate cements in the mouth. The compressive strength is also rate and temperature dependent[29] which may in part account for some discrepancies in values of physical properties reported by various investigators. Therefore, it is not possible to compare directly the data given in Table 4 and elsewhere in the literature.

There are not at this time sufficient laboratory data and extended clinical experience to warrant the wholesale substitutions of zinc polyacrylate cements for zinc phosphate cements in dentistry, but certainly limited clinical use is and should be in progress primarily because of the adhesion between zinc polyacrylate cement and enamel.

How the adhesion occurs is not known. Smith[23] believes that polyacrylic acid reacts with calcium on the surface of the enamel and that polyacrylic acid may form complexes with proteins. No evidence is presented to show that a chelation does occur.

The zinc polyacrylate cements are an exciting development and the development of other carboxylate cements is in progress.

Silicate Cement. Silicate cements have been used in dentistry for about a century primarily as a restorative material for use where esthetics and caries prevention are of utmost importance.

When a pulverized complex alumino-silicate glass containing magnesium, fluorine, calcium, sodium and

phosphorous is mixed with an aqueous solution of ortho-
phosphoric acid buffered by aluminum or zinc salts or
both, a hard strong mass results that simulates the
color and optical properties of the tooth.

The chief fault of these cements as a restorative
material is their solubility in the mouth. The average
life of a silicate cement restoration is about 3 to 4
years. Silicate cement restorations disintegrate in a
decay-like manner. That part of a silicate cement
restoration which is in a relatively self-cleansing
area will remain virtually undissolved while that part
which lies in an area where food and other debris
collect will be selectively dissolved. Even then,
there will be comparatively little recurrent decay about
silicate cement restorations probably because of their
high fluoride content and because this fluoride content
decreases the solubility of the enamel in acids.[30]

Specification requirements, composition and values
of pertinent physical properties of some silicate
cements as obtained according to A.D.A. specification
procedures are given in Table 5. One sees that improve-
ments have been made in these cements over the last few

Table 5

Dental Silicate Cements: Composition and Properties

Requirements of revised ADA Specification No. 9 for Dental Silicate Cement (1962–) (9)	Arsenic Content Maximum per-centage by weight	Consistency of mix	Time of setting at 37°C Minutes		Opacity at 24 hours $C_{0.70}$		Solubility and disintegration Maximum Percentage by weight	Compressive strength at 24 hours* Minimum kgf/cm²
			Min.	Max.	Min.	Max.		
	0.0002	Grams of powder in 0.40 ml of liquid to produce a disk of cement 25 ± 1 mm diameter	3	8	0.35	0.55	1.0	1700
(1950–1962)	0.0002	Same	3	8	0.35	0.55	1.4	1620
Range of values for silicate cements on List of Certified Dental Materials (1958) (12)(13)	<0.0002	1.4 ± 0.15	5 ± 1		all within 0.35 – 0.55		1.0 ± 0.3	1770 ± 140
Range of values for silicate cements on List of Certified Dental Materials (1965) (31)	<0.0002	1.5 ± 0.07	5 ± 1		all within 0.35 – 0.55		0.5 ± 0.1	1950 ± 160
C o m p o s i t i o n (22) Powder % by wgt. / Liquid % by wgt. SiO_2 – 39.9 PO_4 – 47.4 Al_2O_3 – 27.7 Al – 2.3 Ca – 5.9 Zn – 5.6 F – 15.4 Na – 6.6 P_2O_5 – 4.0 Ignition loss 0.8 (110°C)	<0.0002	1.3	4.5		0.46		0.6	1370
SiO_2 – 39.7 PO_4 – 48.6 Al_2O_3 – 35.8 Zn – 8.9 Ca – 3.2 F – 11.0 Na – 6.5 P_2O_5 – 3.9 Ignition loss 0.0 (110°C)		1.2	4.0		0.32		2.8	1510

* 1 kgf/cm² = 14.223 psi

decades as reflected by decrease in the maximum
solubility values permitted in the American Dental
Association specification from 2.0% (1938-1950), to
1.4% (1950-1962) to 1.0% (1962-   ), and an increase
in the minimum values permitted for compression strength
from 1260 kgf/cm² (18,000 psi) (1938-1950) to 1620 kgf/
cm² (23,000 psi) (1950-1962) to 1700 kgf/cm² (24,200
psi) (current). The testing time was decreased from
one week to 24 hours in the 1950 revision. This caused
the 24 hour values for solubility to decrease on the
average 0.25% from the one week values and the value for
compressive strength was on the average 100 kgf/cm²
(1420 psi) less at 24 hours than at one week.

The values obtained on retesting the silicate cements
on the List of Certified Dental Materials (as established
by the American Dental Association) in 1958[12] and in
1965,[31] also given in Table 5, reflect the decrease
in solubility and increase in strength of those silicate
cements between 1958 and 1965.

Pulver[32] took the analysis[22] of a commercial
silicate cement powder and liquid (given at the bottom

of Table 5) and calculated the approximate formula:--

Batch Composition of Cement Powder.--per cent by weight

as SiO_2-39.9; Al_2O_3-30.2; CaF_2-4.0; Na_3AlF_6-19.2 and

$Ca(H_2PO_4)_2 \cdot H_2O$-6.7. The liquid composition was by

weight per cent H_3PO_4-41.3; $Zn_3(PO_4)_2$-17.8 and H_2O-40.9.

Pulver[32] concluded that an aqueous solution of citric

acid would be a more appropriate test medium for

solubility than distilled water.

Wilson and his associates explored in exhaustive

and scholarly investigations[33-44] the nature of

silicate cements with special emphasis on modifying

them so that they would endure the rigors of the mouth

environment better than the available ones. He inter-

preted from his results that there is not much probability

of significantly improving silicate cement. There are

just too many circumscribing parameters that relate to

the specific use of silicate cement in dental health

service.

Zinc silico-phosphate cements. The zinc silico-phosphate

cements, as the name implies, are a kind of hybrid

between zinc phosphate cements and silicate cements, but

their properties are closer to the silicate cements.
The zinc silico-phosphate cements are probably the most
durable in the mouth of any of the dental cements based
on phosphoric acid and since they contain large quanti-
ties of fluoride, they are also probably anticariogenic.

Some of the cements are made by incorporating large
quantities of zinc oxide in the silicate cement glass
and at least one has a powder that is a mechanical
mixture of silicate and zinc phosphate cement powders
in an approximate ratio of 9 to 1. Compositions[22] of
each type, respectively, by weight per cent, follow:

Powder: SiO_2 - 14.6; Al_2O_3-15.6; Ca-3.2; F-5.9;
Na-2.9; P_2O_5-2.1; ZnO-53.2; MgO-2.3; H_2O-0.1 and
ignition loss at 120°C-0.1.

Liquid: PO_4-55.7; Al-2.4; Zn-3.1 and Mg-0.7.

Powder: SiO_2-36.5; Al_2O_3-26.3; Ca-5.9; F-12.0;
Na-4.6; P_2O_5-3.2; ZnO-9.4; MgO-0.5; and ignition loss
at 900°C-6.9.

Liquid: PO_4-48.1; Al-1.9 and Zn-4.4.

The requirements of A. D. A. Specification No. 21
for Dental Zinc Silico-phosphate Cement[45] and the test
values[31] for current American and foreign cements are
given in Table 6.

Table 6

Properties of Dental Zinc Silico-Phosphate Cements

Type	Consistency of mix (Diameter of Disk) mm	Time of Setting at 37°C Minutes Min.	Max.	Compressive strength at 24 hours** kgf/cm² Min.	Film Thickness μm Max.	Solubility and Disintegration at 24 hours wt.% Max.	Opacity 24 hours $C_{0.70}$ Min.	Max.	Arsenic Content Max. wt.%
(45) Requirements of ADA Specification No. 21 for Dental Zinc Silico-Phosphate Cement									
I Cementing	25 ± 1	5	9	1400	50	1.5	0.35	0.90	0.0002
II Filling	25 ± 1	3	8	1700	--	1.0	--	--	0.0002
III Dual		5	9	1400	50	1.5	0.35	0.90	0.0002
		3	8	1700	--	1.0	--	--	0.0002
(31) Survey of current cements by the American Dental Association	Grams of powder in 0.4 ml of liquid								
I Cementing (2 cements)	1.0 ± 0.05	12 ± 6		1160 ± 330*	38 ± 2	1.2 ± 0.4	Complied		No trace
II Filling (4 cements)	1.5 ± 0.12	7 ± 3		1470 ± 270*	--	0.6 ± 0.4	Complied		No trace
III Dual (5 cements)	1.2 ± 0.14	10 ± 1		1280 ± 260*	44 ± 2	0.9 ± 0.0	Complied		No trace
	1.5 ± 0.31	5 ± 1		1580 ± 220*	--	0.5 ± 0.1			No trace

* Range

** 1 kgf/cm² = 14.223 psi.

Resin Cements. Composite cements with a plastic binder

such as poly(methyl methacrylate) and inorganic fillers

such as calcium or barium carbonate, quartz, mica,

alumina or calcium tungstate were used to a small extent

for almost 20 years. The mineral filler contents ranged

from 5 to 67 weight per cent.[46] Because of their rela-

tive insolubility, it was believed that the resin cements

would displace zinc phosphate cements as a luting medium.

However, this has not occurred principally because:

(1) they possess a short working interval between com-

pletion of the mixing and seating of the appliance. A

crust forms on the mix quickly as the monomer evaporates;

(2) it is difficult to remove set cement that accumulates

in the spaces between the teeth when an appliance is

being seated; (3) water seeps at the resin cement-tooth

interface; and (4) they cause a more severe reaction on

the pulp than that caused by zinc phosphate cements.

When prepared at a standard consistency the resin

cements had setting times from 4 to 12 minutes, poly-

merization shrinkage from about 3 to 8 per cent by

volume, expansion (caused by water absorption) from

about 0.6 to 1.8 per cent by volume, aqueous solubility

from 0.1 to 0.4 per cent weight loss, optical opacities

from 0.45 to 1.00 $C_{0.70}$ values, film thickness from 10

to 120 μm, a radiopacity of 0.8 to 2.9 film density on

a 2 mm thick specimen, and compressive strength from

527 to 879 kgf/cm^2 (7,500 - 12,500 psi).[46]

The resin composite cements are adhesive to tooth

enamel if the tooth is kept dry. Otherwise, water

penetrates along the resin cement-enamel interface and

rapid separation of the cement from the enamel occurs.[46]

Direct Filling Resins, Composite and Adhesive Materials.

During World War II in Germany the auto- or self-

polymerization of dental acrylic resins was induced by

adding a tertiary amine (0.5 to 3%) to methyl methacrylate

and 0.5% benzoyl peroxide to the powdered poly(methyl-

methacrylate) with which it was mixed.[47] Soon there

appeared on the world dental market similar direct filling

resins and many thought there was here at last a replace-

ment for the decades-old silicate cement. But this idea

was short lived because the direct resin restorations

discolored, leaked, caused severe pulp response, and

allowed a high incidence of recurrent decay. For these reasons they were abandoned by a great many practitioners. Improvement made by the substitution of N, N-dimethyl-p-toluidine for the previously-used tertiary amines gave less discolored reaction products and the use of p-toluene sulfinic acid as an initiator to decompose the organic peroxide gave even better results. Later, ultraviolet absorbers were added to the formulations so that most present-day direct filling resins and composites have reasonably good color stability in the mouth.

After these relatively simple self-curing direct resin filling materials came the modern composites which are partially displacing silicate cement. The composites are based upon a three component system as illustrated in Table 7 but adhesive cavity primers are largely in the research and testing state.

The addition of the reinforcing fillers with an appropriate coupling agent to bond the inorganic filler to the polymer matrix improved the direct filling resins. The volumetric shrinkage on polymerization was halved, the compressive strength was doubled, and the modulus of elasticity was increased about six fold (Table 8).

Table 7

Modern composite restorative materials

Component	Contents*
Liquid	Monomers Stabilizers Accelerator UV absorber
Powder	Inorganic filler, treated with a silane coupling agent Benzoyl peroxide
Cavity primer	Coupling agent for improving the bond between filling material and hard tooth tissue

* These basic ingredients are supplied commercially
  in various forms, such as paste-liquid, paste-
  paste or powder-liquid, formulated as two or more
  components that are mixed prior to use.

Table 8

Properties of composite dental restorative materials as compared with
direct filling resins, human enamel and dentin

Material	Volumetric shrinkage on polymerization	Compressive strength *	Tensile strength*	Modulus of elasticity*	Indentation resistance[54]	
					Depth	Recovery
	%	kgf/cm²	kgf/cm²	kgf/cm² x 10⁻⁶	μm	per cent
Silica-reinforced polymer as developed by Bowen [48]	2.8	1600	280	0.1125	55	77
Direct filling resin [48]	6.2	750	280	0.0183	95-115 [54]	60-80 [54]
Human dentin (49-51,53)	--	2100-3940	530	0.0844-0.1968	46 (48)	85 (48)
Human enamel (50-53)	--	980-3940	105	0.0914-0.8577	33 (48)	86 (48)

* 1 kgf/cm² = 14.223 psi.

In addition, the coefficient of thermal expansion was
reduced from about 120 x 10^{-6}/°C, to from 40 to 18 x 10^{-6}/°C /[30-40°C (86-104°F)]
while that of the tooth crown (enamel and dentin) is
about 10 or 11 x 10^{-6}/°C. Other properties of the hard
tooth tissues are also presented in Table 8.

To the best of the author's knowledge all of
currently successful filling resins are acrylic resins
or are adducts of acrylic, principally methacrylates,
with other resins. The reason for this is that the
acrylic resins, principally methacrylates, most nearly
meet the circumscribing dental requirements as listed
in Table 9. It is not feasible to indicate these
requirements in the order of their importance. For
example, a resin may be perfect in all respects except
that it is black--and therefore, totally unacceptable
for restoring a front tooth in which esthetic require-
ments are paramount.

Many resins have been developed and tested but have
not reached commercial production. Among these are:
(1) Polystyrene which was injected into tooth cavities.
The restorations failed because of poor marginal integrity.[55]

Table 9

Dental Requirements of Plastic Filling Materials

1.   Polymerizable in the mouth environment.

1.1   Suitable mixing, working and setting times.

1.2   Ease of placing and finishing.

1.3   Minimal residual monomer.

2.   Optical characteristics that permit a formulation
      that simulates the tooth.

2.1   Color match with the tooth.

2.2   Opacity similar to that of the tooth.

2.3   Matching index of refraction.

2.4   Resistance to staining in the mouth by foods,
      tobacco smoke, cosmetics and bacterial products.

2.5   Color stability in the mouth.

3.   Biocompatibility and preventive capacity.

3.1   Not seriously irritating to the pulp and to the gingiva.

3.2   Low systemic toxicity.

3.3   General passivity.

3.4   Anticariogenic properties.

4.   Dimensional stability.

4.1   Low polymerization shrinkage.

4.2   Low dimensional change on absorbing water.

4.3   A coefficient of thermal expansion as close
      to that of the tooth as possible $(10 \times 10^{-6}/°C)$.

4.4   Minimum change on release of stress on absorption
      of water.

5.   Adequate mechanical properties.

5.1   Strength.

5.2   Elastic modulus.

5.3   Elastic limit.

5.4   Indentation resistance and recovery.

6.   Adequate physical properties.

6.1   Abrasion resistance to food, dentifrices and teeth.

6.2   Softening point higher than temperatures
      encountered in the mouth.

7.   Adhesive to tooth tissues.

8.   Insolubility.

9.   Low water absorption

10.   Adequate shelf life.

11.   Radiopacity.

(2) Polyamide, which was also injected into tooth cavities but was discontinued because the restorations failed cosmetically.[55] (3) An aziridino polyester composite that was introduced commercially in 1959 under the trade name of "Cadurit" had relatively poor physical properties.[56] After a three year clinical trial it showed poor color stability and surface loss.[57,58] This material had inferior physical properties compared to those of poly(methyl methacrylate) as determined in the laboratory and had inferior clinical behavior--a reasonably good correlation. Cadurit is an example of a filling material being placed upon the market seemingly without adequate laboratory or clinical testing. (4) A polycarbonate that was softened and injected into tooth cavities.[58] It maintained reasonable marginal accuracy and was color stable. The material never reached commercial production although one large company in Germany made an injection apparatus for its use. The material would be, in the author's opinion, unable to compete commercially with current dental restorative

materials because of the technic involved. (5) Epoxy
resins were thought to have possibilities as a direct
filling resin. At least one company attempted to
fabricate an epoxy material but it could not be used
clinically because moisture interfered with its poly-
merization and the dentin surface could never be made
moisture-free.[59] (6) Cyanoacrylates, none of which
have proved successful as a direct filling resin but a
n-butyl-α-cyanoacrylate composite has some possibilities
as a dental cementing medium.[60] Another cyanoacrylate,
methyl-α-cyanoacrylate, as a component for a composite
used as a fissure sealant in caries prophylaxis had
limited success[61] but has now been abandoned for a
new sealant composite[62] containing the reaction product
of bisphenol A and glycidyl methacrylate[48] and is poly-
merized by UV light.[62] The technic is simple and in
one year of clinical testing only one fissure became
uncovered. All treated teeth were free from decay after
one year, but matched control teeth had caries in 42%
of the pits and fissures.[62]

The outstanding development in the preparation of
a successful composite restorative material to date has
been the work of R. L. Bowen, a research associate from
the American Dental Association at the National Bureau
of Standards.[48,63-67] In his material, the resin
matrix is the addition-reaction product of bisphenol A
and glycidyl methacrylate (BIS-GMA). Viscosity of the
resultant product was lessened when methacrylate monomers,
stabilizer, and accelerator were added. These constituted
the liquid component. The powder consisted of vinyl
silane-coated fused silica and benzoyl peroxide. Another
silane now seems more appropriate.[67] BIS-GMA, while
not completely color stable, is used in almost all of
the commercially available composite restorative materials
made in the U.S.A. The trade names of some of these and
some physical property values from two recent reports[68,69]
are given in Table 10. The methods used in references
68 and 69 were not usually identical which may account
for some of the differences among the data.

One group of workers[69] also reported the water
sorption of the four materials listed in Table 10 as about

Table 10

Physical Properties of Some‡ Commercial Composite Dental Restorative Materials

Brand Name#	Manufacturer	Setting Time	Volumetric Polymerization contraction	Coefficient of thermal expansion†	Indentation Resistance		Strength			Modulus Elastic* //	Reference
					Depth	Recovery	Compressive* //	Tensile* //	Shear //		
		Min.	%	× 10⁶/°C	μm	%	kgf/cm²	kgf/cm²	kgf/cm²	kgf/cm² × 10⁻⁶**	
Addent 35(R)	Minnesota Mining and Manufacturing Co. St. Paul, Minnesota	4.5	1.3	33	65	69.8	1434	330	471	0.0935	(68)
			2.0	45			1462			0.0914	(69)
Addent 12(R)		4.5	1.2	27	77	69.7	2039	415	696	0.1139	(68)
			3.1	43			2137			0.1125	(69)
Dakor(R)	Caulk Division of Dentsply International Inc., York, Penna.	1.5	1.5	41	97	62.3	1223	141	302	0.0548	(68)
			3.5	50			1115	244		0.0703	(69)
Adaptic(R)	Johnson and Johnson, New Brunswick, N.J.		1.5	22						0.1195	(69)

‡ Similar materials having similar values are Blendant, manufactured by Kerr-Sybron Corporation, Detroit, Michigan; DFR, manufactured by Surgident Ltd., Los Angeles, California and Posite, manufactured by American Consolidated Manufacturing Co., Inc. Philadelphia, Penna.

Color stability was reported as "change" in (68) and (69) in all the brands, except (68) reported "no change" in Dakor. (R)

* 30 days in water at 37°C.

** The values were inadvertently reported as 10³ lb/in² in (68) and as psi × 10⁵ in (69).

† Temperature range in (68) was 24-88°C; in (69) possibly 0-52°C. The linear values given in (69) were converted to volumetric values by multiplying by 3.

// 1 kgf/cm² = 14.223 psi.

1.5% weight gain for Addent 35, 1.0% for Addent 12,
0.75% for Adaptic. The Dakor specimens during the
sorption test declined 3% in weight. The solubility
was about 3% for Dakor, about 1% for Addent 12, 0.5%
for Addent 35, 0.25% for Adaptic. The author is not
aware of any clinical investigations that might reflect
the foregoing laboratory findings or those reported in
Table 10. Comparisons are also difficult since there
is no American Dental Association specification for
the resin composite restorative materials, but standard
test methods have been adopted for specimen preparation,
indentation resistance and recovery, opacity and Knoop
indentation hardness.[70] Other proposed tests are
being prepared for abrasion and abradability, adhesion,
dimensional change on hardening, on absorption of water
and on change in temperature, extractible plasticizer,
time of setting, sorption and solubility. All of
the foregoing are being woven into a future specification
of the American Dental Association for composite dental
restorative materials.

A new development involving three crystalline dimethacrylate monomers[71] with melting points slightly above room temperature, which liquefy in ternary eutectic proportions, seems suitable for composite formulations. The three monomers synthesized by Bowen are: bis(2-methacryloxyethyl)isophthalate, (MEI); bis(2-methacryloxyethyl)terephthalate, (MET) and bis(2-methacryloxyethyl)-phthalate (MEP). They are condensation products of 2-hydroxyethyl methacrylate (HEMA) and the corresponding acid chlorides of the phthalic acid position isomers.[71] The approximate ternary eutectic proportions, 47% (MEI), 38% (MEP), and 15% (MET) melt at about 16°C. Since the monomers are crystalline, they are relatively easy to purify and since the ternary eutectic is a nonvolatile liquid of a suitable viscosity at room temperatures and has a very low toxicity, it was used in the formulation of a resin composite which is now undergoing clinical trials. The Epoxylite Corporation, P. O. Box 3397, South El Monte, California 91733 has synthesized these methacrylate monomers in custom batches.

Reinforcing fillers, (bonded to the resin matrix by a coupling agent) that have been advocated or used in resin composite restorative materials include fused silica, quartz, beta-eucryptite ($LiAlSiO_4$), glass beads and rods, "tricalcium phosphate"[72] and certain porcelain and ceramic materials. The latter, also called micro-crystalline glasses, have attractive properties such as high translucency, favorable refractive indexes and thermal expansion coefficients approximating zero.

Adhesives. None of the dental restorative materials are adhesive to untreated human enamel and dentin, which they abut, with the possible exception of a methacrylate resin in which an alkylboron compound, such as tri-n-butylboron, is used as a hardening agent.[73] An experimental material of this type has been tested clinically with evidence of adherence to the dentin, but not in every case, so the usual retentive undercuts in preparations for plastic restorations cannot be omitted.[74]

In designing a restorative material that will adhere to enamel and dentin under mouth conditions or in design-ing a cavity primer which would serve as a coupling agent

between enamel and dentin and restorative materials, it is necessary to have extensive knowledge about calcified tooth tissues. These tissues are really natural composites as they consist of associated organic and inorganic portions in a structural entity with remarkable qualities. The organic portion of dentin is about 20% by weight, almost all of it being collagen, with fractional percentages of carbohydrate and lipids. In enamel, the organic content is less than 0.5 per cent. The major inorganic content of enamel and dentin is hydroxyapatite. Other ions such as sodium, potassium, chloride, fluoride, carbonate and citrate are present but their exact relationship with hydroxyapatite is not completely understood.

The cut surfaces of the cavity preparation are moist and are covered by debris from the machining involved. Various treatments have been used to prepare this surface for the reception of an adhesive. Acids, alkalis, enzymes and sequestrants have been used to "clean" the cavity surface by removal of the loose or partially attached debris as well as to remove selectively some of the organic or the inorganic portion of the dentin and enamel. These pretreatments usually

enhance the adhesion as measured by mechanical tests
of various types. Adhesion test methods need to be
standardized so comparable values in the literature
will have some relevance to each other. The enhancement
of the adhesion by the pretreatment of the surfaces of
the tooth is probably in part not only due to removal
of the debris but also due to selective dissolving of
some of the components of enamel and dentin thus pre-
senting a much greater surface area as well as a much
more reactive one. In addition, the removal of material
will not always be in parallel directions and thus there
will be undercuts available into which the low-surface-
tension monomers can flow. Hence, on polymerization,
there will be considerable mechanical retention as well
as retention from any chemical bonding that may occur.[75]

A cavity primer, if it is a successful coupling
agent that bonds the hard tooth tissues to the restorative
material, must have chemical groups that will react with
the tooth surface and the hardening resin and that will
compete with the always-present water at the interface
between the cavity surface and the composite restorative

material. The bond must be strong enough to withstand
the stresses induced by polymerization, by subsequent
water absorption and by the differential in thermal
expansion of the tooth and the restorative material.
The stresses induced by polymerization of direct filling
resins ranged from about 28 kgf/cm² (400 psi) to 134 kgf/
cm² (1900 psi) depending upon the geometry of the
cavity.[76] The values for stresses induced or relieved
by water absorption or by differential thermal expansion
of the interface materials have not been found in the
literature by the author.

There is a possibility that the stresses induced by
bonding at the interface may be undesirable. Consequently
a resilient type of acrylic or epoxide cavity primer has
been investigated.[77] To the best of the author's knowledge,
cavity primers of these types[77] have not appeared on
the dental market.

Another development that has promise but has not
yet reached commercial development is an adduct of
N-phenyl glycine and glycidyl methacrylate.[78] Tensile
bond strength values using this adduct between a dental

restorative composite material and enamel, dentin and fluorapatite (treated with a 10% aqueous solution of the sodium salt of ethylenediaminetetraaceticacid) were 55 kgf/cm² (780 psi), 26.7 kgf/cm² (380 psi) and 41 kgf/cm² (580 psi), respectively. It is now under experimental clinical trial.

Workers at the Gillette Research Institute first suggested[79] and have done considerable research on cavity primers based on polyurethanes.[80] In these reports,[79,80] several polyurethane-type compositions were used to couple dentin to a variety of restorative materials--amalgam, cement, direct filling resins and composites. A typical adhesive was prepared from equal parts by weight of tolylene diisocynate (TDI) and a polypropylene glycol. Sometimes 0.01 per cent of tri-propylamine was used as a catalyst. Other isocyanates and a number of polyglycols were used. Several adhered well to dentin and to a variety of restorative materials, were water resistant and performed well in thermal shock, tensile and compressive adhesion tests.[79] Later, reinforcing fillers such as titanium dioxide were used

to dilute the brown color of the polyurethanes as well
as to increase the adhesive strength, as did etching
with 50 per cent solutions of formic or citric acids.
The preferred polyurethanes were compounded principally
from refined castor oil and polymethylene polyphenyl
isocyanate (PAPI) which, with the TiO_2 filler and etching
and debridement treatments of bovine enamel surfaces,
gave butt joint strengths of about 91 kgf/cm² (1300
psi).[80]

Other work, carried out by the Epoxylite Corporation,
gave a preferred formulation of a cavity primer entitled
NIH-302S-1 and consisting of:

Part A	Parts by weight
MDI (diphenylmethane-4, 4'-diisocyanate)	100

Part B	
Polybutadiene diol	5.0
Dibutyl tin laurate	0.575
Chloroform	94.425

Equal parts of A and B were mixed and applied to
bovine enamel (pretreated by etching for five minutes

with a 50% solution of citric acid) with a cotton
applicator and allowed to dry for five minutes. A
tensile bond strength of about 92 kgf/cm^2 (1500 psi)
was obtained on specimens of bovine enamel-... ...mer-
composite restorative material, the latter containing
82 per cent of inert filler.[81]

There has been some in vitro testing of polyurethanes
as cavity primers. A polyurethane varnish was used as a
cavity primer for 40 amalgam restorations which were then
submerged in a fluorescent dye solution and cycled
0-37°-70°C. The microleakage was minimal.[82]   Other
formulations, using reacted products of various isocyanates
and prepolymers with isocyanate end groups and with an
excess of 2-hydroxyethyl methacrylate or the addition
product of bisphenol A and glycidyl methacrylate, did
not bond to tooth structure after one week in water and
softened and darkened during storage in water.[83]

Inorganic polymers. Other than glasses and glass-like
ceramics, no inorganic polymers seem to have dental applica-
tion as restorative materials as revealed by an extensive
and excellent review.[84]

Radiopaqueness. All materials used as operative or prosthetic restorative materials should be radiopaque so that they may be located radiographically if accidentally ingested or aspirated. To achieve radiopacity without destroying the life-like appearance of restorative materials was not accomplished until clear, colorless glasses were developed with an index of refraction near that of the suitable available synthetic resins and having elements with relatively high atomic numbers to give the desired radiopacity. At the same time it was necessary that these glasses be suitable as reinforcing fillers for dental restorative composite materials.[85] These glasses were prepared by melting together compounds yielding silica, boric oxide, alumina, barium oxide and barium fluoride. Barium made the glasses radiopaque, fluoride lowered the refractive indexes and alumina tended to stabilize the glasses.[85]

Biocompatibility. Dental restorative materials are usually placed against crown dentin, the calcified tissue between the thin enamel cover of the crown of the tooth and the pulp chamber in the center, which is normally

filled with soft tissues, blood and lymph vessels and

nerves. The dentin is not solid but is filled with

small canals containing extensions of dentin forming

cells (odontoblasts) which line the pulp chamber. When

the dentin is cut in cavity preparation these fibrils

are also cut and some injury occurs to the odontoblasts.

If an irritant or toxic substance is placed against the

dentin, further injury or even death of the odontoblasts

may take place. Therefore, the restorative material

which is placed against the dentin should not irritate

the pulp unduly. Most materials cause some injury but

this injury is usually resolved and the odontoblasts

recover and lay down additional dentin as they retreat.

This dentin, sometimes called secondary dentin, is con-

sidered by some investigators but not by others as an

effective barrier against further injury.

The transient and prolonged effects of most of the

dental restorative materials in this review have been

reported by a host of investigators using rat, dog,

monkey and human teeth. Similar effects were observed

on all of the foregoing. A rough rating of severity from

the least to the most severe gives the following appro-
ximate order: (1) zinc oxide-eugenol based cements;[86,87]
(2) zinc polyacrylate cements;[23],[88] (3) zinc phosphate
cement;[89] (4) zinc silico-phosphate cement; (5) res-
torative composites;[90] (6) silicate cements;[91] (7)
direct filling resins;[92] resin cements;[93] and (8)
black copper cements.[94] The earlier references have
been given. Much confirmatory work has since been done
and most of the work confirms that zinc oxide-eugenol
cement is the blandest with almost no irritation and
that black copper cements produce the most severe reaction.
The foregoing order of arrangement is very relative and
should not be taken too literally but in all of the
materials cited except zinc oxide-eugenol based cements,
and perhaps the zinc polyacrylate cements, an intermediary
lining should be present between the restorative material
and the dentin to protect the pulp.[95]

Bioevaluation. As new materials are being developed so
rapidly, it is imperative that adequate bioassays be made.
In the case of dental restorative materials this bio-
evaluation procedure has not been completely worked out

but the following have been suggested:[96] (1) an

acute systemic toxicity test of the type known as LD_{50}

in which the dose of the material ingested, in grams

per kilogram of body weight of the rat, will cause a

50 per cent mortality in 14 days; (2) a mucous membrane

irritation test on non-rodent animals in which the

material in question is held for 2 weeks in contact with

the mucous membrane. The degree of irritation is judged

by gross appearance as observed visually and by color

photographs and by biopsy of tissues in and out of contact

with the material; (3) a test for pulp irritation in which

at least 30 teeth from middle aged patients are restored

with the material and 30 similar untreated control teeth

are available. Serial extraction of the teeth

are made at 24 hours, 10 to 30 days and after 60 days,

respectively. After preparation for histologic examination,

serial sections are examined using twelve criteria and the

restored and controlled teeth compared. Also, guide lines

are being set up for the clinical comparison of restorative

materials.

Mouth conditions. The mouth is a rigorous environment
so only relatively passive materials such as noble metal
alloys, chromium-based alloys, porcelain and organic
polymers can resist the attack of foods and microbial
metabolic products.

Recurrent decay and anticariogenic properties: Recurrent
decay at the tooth-filling margin or at the cavity surface-
filling interface frequently occurs and especially in
persons with poor dental hygiene. Therefore, an ideal
restorative material should have anticariogenic properties.
Silicate cement is almost unique among the dental restora-
tive materials in this respect because there is almost no
recurrent decay around silicate cement restorations. One
study showed that the direct filling resins had about
10 per cent recurrent caries after three years and no decay
occurred around silicate cement restorations used as
controls.[97] It is believed that the anticariogenic pro-
perties of silicate cement stem from its release of fluoride
to the enamel which decreases the enamel solubility.[30]

Allergy. Allergic responses have been cited for all of
the restorative materials employed in dentistry but the

number of responses is only a very small part of one

per cent. This will hold true for countless substances

with which humans come in contact.

Source references. Extensive information is presented for zinc

oxide-eugenol cements,[4] EBA cements,[98] zinc phosphate

cements,[14] copper phosphate cement,[20] zinc poly-

acrylate cements,[23-29] silicate cement,[22,33-44] zinc

silico-phosphate cements,[22,31,45] resin cements,[46]

composite restorative materials,[57,62,67,68] dental

adhesives,[62,78,80] inorganic polymers,[84] and pulp

reactions to restorative materials.[95] In addition,

the following general sources are recommended: 99-112.

References

1. Copeland, H. I. Jr., Brauer, G. M., Sweeney, W. T. and Forziati, A. F. Setting reaction of zinc oxide and eugenol. J. Res. Nat. Bur. Stand., 55:133 Sept. 1955.

2. Brauer, G. M., White, E. L. Jr. and Moshonas, M. G. The reaction of metal oxides with o-ethoxybenzoic acid and other chelating agents. J. of Dent. Res. 37:547, June 1958.

3. Brauer, G. M., McLaughlin, R. and Huget, E. F. Aluminum oxide as a reinforcing agent for zinc oxide-eugenol-o-ethoxybenzoic acid cements. J. of Dent. Res. 47:622 July-Aug. 1968.

4. Brauer, G. M. A review of zinc oxide-eugenol type filling materials and cements. Rev. Belge. Med. Dent. Tijds.Vr Tandheel, 20:323 Nov. 1965.

5. Wallace, D. A. and Hansen, H. L. Zinc oxide-eugenol cements. J. Amer. Dent. Ass. 26:1536 Sept. 1939.

6. Paffenbarger, G. C. and Caul, H. J. Dental
    cements. Proc. Dent. Centenary Session p.232-237,
    March 1940. Waverly Press, Baltimore, Md.

7. Phillips, R. W. and Love, D. R.   The effect of
    certain additive agents on the physical properties
    of zinc oxide-eugenol mixtures. J. of Dent. Res.
    40:294, Mar.-Apr. 1961.

8. Anderson, J. R. Jr. and Myers, G. E. Physical
    properties of some zinc oxide-eugenol cements.
    J. of Dent. Res. 45:379, Mar.-Apr. 1966.

9. Guide to Dental Materials, American Dental Associa-
    tion, 211 East Chicago Ave., Chicago, Ill. 60611,
    4th Ed. 1968-1969.

10. Crowell, W. S. Physical chemistry of dental
    cements. J. Amer. Dent. Ass. 14:1030, June 1927.

11. Guide to Dental Materials, American Dental Associa-
    tion. (see reference 9 for address). 3rd Ed. 1966.

12. Paffenbarger, G. C. and Stanford, J. W. Zinc
    phosphate and silicate cements. Dent. Clin. N.
    Amer. Nov. 1958, p.561.

13. Council on Dental Research, List of Certified
    Dental Materials revised to April 1, 1958. J.
    Amer. Dent. Ass. 56:752, May 1958.

14.   Paffenbarger, G. C., Sweeney, W. T. and Isaacs,
        A. Zinc phosphate cements: physical properties
        and a specification. J. Amer. Dent. Ass. 21:
        1907, Nov. 1934.

15.   Simmons, F. F., D'Anton, E. W. and Hudson, D. C.
        Property studies of a hydrophosphate cement.
        J. Amer. Dent. Ass. 76:337, Feb. 1968.

16.   Kinjo, K. Studies on the improvement of water-
        settable phosphate cement. An examination of
        various production methods of primary phosphate
        salt. J. Jap. Res. Soc. Dent. Mater. Appl. 16:
        144, April 1967. (Abstract in English.) (See
        also Oral Research Abstracts 2:737, Sept. 1967.)

17.   Higashi, S. Concerning water-setting zinc phos-
        phate cement. J. Jap. Dent. Ass. 15:743, Jan.
        1963.

18.   Nagai, K. and Katoh, M. A new zinc phosphate
        cement employing water as a liquid. (Report given
        at the 52nd Annual Session of the Federation
        Dentaire Internationale, San Francisco, Calif.
        1964.) (Unpublished--see discussion in Internat.
        Dent. J. 15:357, Sept. 1965.)

19. Takeuchi. M. Studies on an improvement of water-settable phosphate cements--with reference to the development of a new ingredient as primary phosphate polymer. J. Jap. Res. Soc. Dent. Mater. Appl. 16:115 April 1967. (Abstract in English.) (See also Oral Research Abstracts 2:737. Sept. 1967.)

20. Worner, H. K. The physical and mechanical properties of "copper" cements. Aust. Dent. J. 44:411, Dec. 1940 and 45:1, Jan. 1941.

21. Paffenbarger, G. C. and Beall, J. R. American Dental Association Specification No. 8 for Dental Zinc Phosphate Cement--First Revision (effective July 1, 1938). J. Amer. Dent. Ass. 24:2019, Dec. 1937.

22. Paffenbarger, G. C., Schoonover, I. C. and Souder, W. Dental silicate cements: physical and chemical properties and a specification. J. Amer. Dent. Ass. 25:32, Jan. 1938.

23. Smith, D. C. A new dental cement. Brit. Dent. J. 125:381, Nov. 15, 1968.

24. Mortimer, K. V. and Tranter, T. C. A preliminary laboratory evaluation of polycarboxylate cements. Brit. Dent. J. 127:365, Oct. 21, 1969.

25.   Mizrahi, E. and Smith, D. C.   Studies of the adhesion of orthodontic brackets to enamel using a polyacrylate cement.   J. of Dent. Res. 47: 999, Nov.-Dec.1968.   No. 6 Abstract.

26.   Mizrahi, E. and Smith, D. C.   Direct cementation of orthodontic brackets to dental enamel.   Brit. Dent. J. 127:371, Oct. 21, 1969.

27.   Mizrahi, E. and Smith, D. C.   The bond strength of a zinc polycarboxylate cement: investigations in the behavior under varying conditions.   Brit. Dent. J. 127:410, Nov. 4, 1969.

28.   Smith, D. C.   The effect of variations in composition on the properties of polyacrylate (polycarboxylate) cements.   Program and abstracts of papers, 1970 General Meeting, International Association for Dental Research, 211 East Chicago Avenue, Chicago, Illinois 60611 (Abstract 796, page 248).

29.   Jurecic, A. and Fairhurst, C. W.   Mechanical and viscoelastic properties of a polycarboxylate cement. Program and abstracts of papers, 1970 General Meeting, International Association for Dental Research, Chicago, Illinois (Abstract 794, p. 247). (See reference 28 for address.)

30. Phillips, R. W. and Swartz, M. L. Effect of certain restorative materials on solubility of enamel. J. Amer. Dent. Ass. 54:623, May 1957.

31. Personal communication from Dr. John W. Stanford, Secretary, Council on Dental Materials and Devices, American Dental Association. (see reference 9 for address).

32. Pulver, J. C. The solubility of a dental silicate cement. Master's thesis. Alfred University, Alfred, N. Y. Oct. 1968.

33. Wilson, A. D. and Batchelor, R. F. Dental silicate cements: I. The chemistry of erosion. J. of Dent. Res. 46:1075, Sept.-Oct. 1967.

34. Wilson, A. D. and Batchelor, R. F. Dental silicate cements: II. Preparation and durability. J. of Dent. Res. 46:1425, Nov.-Dec. 1967.

35. Wilson, A. D. and Batchelor, R. F. Dental silicate cements: III. Environment and durability. J. of Dent. Res. 47:115, Jan.-Feb. 1968.

36. Wilson, A. D., Kent, B. E. and Batchelor, R. F. Dental silicate cements: IV. Phosphoric acid modifiers. J. of Dent. Res. 47:233, March-April, 1968.

37. Wilson, A. D. and Kent, B. E. Dental silicate cements: V. Electrical conductivity. J. of Dent. Res. 47:463, May-June, 1968.

38. Wilson, A. D. and Mesley, R. J. Dental silicate cements: VI. Infrared studies. J. of Dent. Res. 47:644, July-Aug. 1968.

39. Wilson, A. D. Dental silicate cements: VII. Alternative liquid cement formers. J. of Dent. Res. 47:1133, Nov.-Dec. 1968.

40. Kent, B. E. and Wilson, A. D. Dental silicate cements: VIII. Acid base aspect. J. of Dent. Res. 48:412, May-June 1968.

41. Wilson, A. D. and Kent, B. E. Dental silicate cements: IX. Decomposition of the powder. J. of Dent. Res. 49:7, Jan.-Feb. 1970.

42. Wilson, A. D. and Kent, B. E. Dental silicate cements: X. The precipitation reaction. J. of Dent. Res. 49:21, Jan.-Feb. 1970.

43. Kent, B. E., Fletcher, K. E. and Wilson, A. D. Dental silicate cements: XI. Electron probe studies. J. of Dent. Res. 49:86, Jan.-Feb. 1970.

44. Wilson, A. D., Kent, B. E., Batchelor, R. F., Scott, B. G. and Lewis, B. G. Dental silicate cements: XII. The role of water. J. of Dent. Res. 49:307, March-April 1970.

45. Reports of Councils and Bureaus. New American Dental Association Specification No. 21. Adopted. J. Amer. Dent. Ass. 78:577, March 1969.

46. Schouboe, P. J., Paffenbarger, G. C. and Sweeney, W. T. Resin cements and posterior-type direct filling resins. J. Amer. Dent. Ass. 52:584, May 1956.

47. Fiat Final Report No. 1185, Recent German developments in the field of dental resins. Office of Military Government for Germany (US) Field Information Agency, Technical 27, May 1947.

48. Bowen, R. L. Properties of a silica-reinforced polymer for dental restorations. J. Amer. Dent. Ass. 66:57, Jan. 1963.

49. Craig, R. G. and Peyton, F. A. Elastic and mechanical properties of human dentin. J. of Dent. Res. 37:710, Aug. 1958.

50. Stanford, J. W., Paffenbarger, G. C., Kumpula, J. W. and Sweeney, W. T. Determination of some compressive properties of human enamel and dentin. J. Amer. Dent. Ass. 57:487, Oct. 1958.

51.   Stanford, J. W., Weigel, K. V., Paffenbarger, G. C.
       and Sweeney, W. T. Compressive properties of
       hard tooth tissues and some restorative materials.
       J. Amer. Dent. Ass. 60:746, June 1960.

52.   Craig, R. G., Peyton, F. A. and Johnson, D. W.
       Compressive properties of enamel, dental cements
       and gold. J. of Dent. Res. 40:936, Sept.-Oct. 1961.

53.   Bowen, R. L. and Rodriguez, M. S. Tensile strength
       and modulus of elasticity of tooth structure and
       several restorative materials. J. Amer. Dent. Ass.
       64:378, March 1962.

54.   Sweeney, W. T., Sheehan, W. D. and Yost, E. L.
       Mechanical properties of direct filling resins.
       J. Amer. Dent. Ass. 49:513, Nov. 1954.

55.   Jarby, S. Thermoplastified synthetic resin
       (polystyrene) as a dental filling material.
       Odont. Tidskr. 67:242, Nov. 3, 1959.

56.   McLean, J. W. Some physical properties of a new
       cross-linked plastic filling material. Brit.
       Dent. J. 110:375, June 6, 1961.

57. McLean, J. W. and Short, I. G. Composite anterior filling materials: A clinical and physical appraisal. Brit. Dent. J. 127:9, July 1, 1969.

58. Jarby, S. and Erikson, K. Dental fillings of polycarbonate and of "Cadurit". Odont. Tidskr. 72:487, 1964.

59. McLean, J. W. Anterior filling materials in Europe. Dent. Prog. 2:181, April 1962.

60. Civjan, S., Margetis, P. M. and Reddick, R. L. Properties of n-butyl-α-cyanoacrylate mixtures. J. of Dent. Res. 48:536, July-Aug. 1969.

61. Cueto, E. I. and Buonocore, M. G. Sealing of pits and fissures with an adhesive resin: its use in caries prevention. J. Amer. Dent. Ass. 75: 121, July 1967.

62. Buonocore, M. Adhesive sealing of pits and fissures for caries prevention with use of ultra-violet light. J. Amer. Dent. Ass. 80:324, Feb. 1970.

63. Bowen, R. L. Investigation of the surfaces of hard tooth tissues by a surface activity test. Proc. Workshop on Adhesive Restorative Dental Materials, Indiana University. Owen Litho Service, Spencer, Indiana, 1961.

64.   Bowen, R. L. Dental filling material comprising
       vinyl silane treated fused silica and a binder
       consisting of the reaction product of bisphenol
       and glycidyl acrylate. U. S. Patent No. 3,066,112,
       November 1962.

65.   Bowen, R. L. Method of preparing a monomer having
       phenoxy and methacrylate groups linked by hydroxy-
       glyceryl groups. U. S. Patent No. 3,179,623,
       April 1965.

66.   Bowen, R. L. Silica-resin direct filling material
       and method of preparation. U. S. Patents No.
       3,194,783 and 3,194,784, July 1965.

67.   Bowen, R. L. Development of an adhesive restora-
       tive material. Adhesive Restorative Materials
       II. Proceedings from the second workshop sponsored
       by the Biomaterials Research Advisory Committee,
       National Institute of Dental Research, Bethesda,
       Maryland, 20014, 1965, p. 225.

68.   Macchi, R. L. and Craig, R. G. Physical and
       mechanical properties of composite restorative
       materials. J. Amer. Dent. Ass. 78:328, Feb. 1969.

69.   Lee, H. L. Jr., Swart.   ... and Smith, E. H.
        Physical properties of four thermosetting dental
        restorative resins. J. of Dent. Res. 48:526,
        July-Aug. 1969.

70.   Reports of Councils and Bureaus, Council on
        Dental Materials and Devices, Standard test methods
        for direct filling resins. J. Amer. Dent. Ass.
        75:1426, Dec. 1967.

71.   Bowen, R. L. Crystalline dimethacrylate monomers.
        J. of Dent. Res. 10:810, July-August 1970.

72.   Phillips, R. W. Report of the committee on
        scientific investigation of the American Academy
        of Restorative Dentistry. J. Prosth. Dent. 19:
        416, April 1968.

73.   Masuhara, E., Tarume, Z. and Nakabayashi, N.
        Studies on self-curing resins (5): Comparison with
        some alkylborons as initiator for self-curing
        resins. Reports of the Research Institute of
        Dental Materials, Tokyo Dental and Medical
        University, 2:622, March 1965.

74. Lenz, H. and Viohl, J. Werkstoffkundliche Untersuchungen mit einen neuen Kunststoff-Füllungs-material. Deut. Zahnaerztl. Z. 2:218, Feb. 1968.

75. Buonocore, M., Matsui, A. and Gwinnett, A. J. Penetration of resin dental materials into enamel surfaces with reference to bonding. Arch. Oral Biol. 13:61, Jan. 1968.

76. Bowen, R. L. Adhesive bonding of various materials to hard tooth tissues. VI. Forces developing in direct filling materials during hardening. J. Amer. Dent. Ass. 74:439, Feb. 1967.

77. Patrick, R. L. and Kaplan, C. M. Rubbery polymers as intermediate layers between tooth structure and restorative materials. Adhesive Restorative Materials-II. Proceedings from the second workshop sponsored by the Bio-Materials Research Advisory Committee, National Institute of Dental Research, Bethesda, Maryland 20014, 1965, p. 156.

78. Bowen, R. L. Adhesive bonding of various materials to hard tooth tissues, IV. Bonding to dentin, enamel and fluorapatite improved by use of a surface-active comonomer. J. of Dent. Res. 44: 906, Sept.-Oct. 1965.

79. Galligan, J. D., Schwartz , A. M. and Minor,
     F. W. Adhesive polyurethane liners for
     anterior restorations. J. of Dent. Res. 47:
     629, July-Aug. 1968.

80. Ellison, A. H. and Fookson, H. Adhesive
     restorative dental materials. Annual Compre-
     hensive Report-1969 to the National Institute
     of Dental Research. (Clearinghouse No. PD188-781.)
     National Technical Information Service ,
                Springfield, Virginia 22151.

81. Lee, H., Swartz, M. and Schubert, R. Final
     report on adhesive restorative dental materials.
     April 27, 1970, to the National Institute of
     Dental Research. (Clearinghouse number not
     assigned as of July 10, 1970.)
      National Technical Information Service ,
     Springfield, Virginia 22151.

82. Stark, M. M., Soelberg, K. B., Nicholson, R. J.
     and Johnson, B. Marginal seal afforded by poly-
     urethane varnish as a cavity liner. Program and
     abstracts of papers- 1970 General Meeting of the
     International Association for Dental Research,
     Chicago, Illinois (Abstract 412, p.151).

83. Buonocore, M. G. and Casciani, C. A. Synthesis
and properties of certain urethanes of potential
use in restorative dentistry: a preliminary report.
N. Y. State Dent. J. 35:135 March 1969.

84. Venezky, D. L. Adhesive restorative dental
materials: a literature survey of inorganic
polymers. NRL Report 6294, U. S. Naval Research
Laboratories, Washington, D. C. (Clearinghouse
No. AD620156).

 National Technical Information Service, Springfield,
Virginia 22151.

85. Bowen, R. L. and Cleek, G. W. X-ray-opaque
reinforcing fillers for composite materials.
J. of Dent. Res. 48:79, Jan.-Feb. 1969.

86. Manley, E. B. A preliminary investigation into
the reaction of the pulp to various filling
materials. Brit. Dent. J. 60:321, April 1936.

87. Manley, E. B. Investigations into the early
effects of various filling materials on the
human pulp. Dent. Rec. 62:1, Jan. 1942.

88. Klötzer, W. T., Dowden, W. E. and Langeland, K.
Evaluation of the physical and biological properties
of polycarboxylate cements. Program and abstracts
of papers, 1970 General Meeting, International
Association for Dental Research, (see reference 28).
(Abstract 795, p.247.)

89. Gurley, W. B. and Van Huysen, G. Histologic changes
in teeth due to plastic filling materials. J. Amer.
Dent. Ass. 24:1807, Nov. 1937.

90. Stanley, H. R., Swerdlow, H. and Buonocore, M. G.
Pulp reactions to anterior filling materials. J.
Amer. Dent. Ass. 75:132, July 1967.

91 Palazzi, S. Die Anatomischen Veranderungen der
Zahnpulpa in Gefolge von Silikatzement Füllungen.
Zeitschrift für Stomatologie 21:379, May 1923.

92. Castagnola, L. Les Obturations en Bouche avec
les Resines Autopolymerisantes, Rev. Belge de
Stom. 49:1, 1952.

93. Langeland, K. Pulp reactions to resin cements.
Acta. Odontol. Scand. 13:239, Feb. 1956.

94. Fish, E. W. Reaction of the dental pulp to peri-
pheral injury of the dentin. Roy. Soc. Med. Sect.
Odont. Proc., London, 108 (Ser.B):196, May 1931.

95.   Massler, M. Effect of filling materials on the
       pulp. J. Tennessee State Dent. Assn. 35:353,
       Oct. 1955.

96.   American National Standards Committee Z156 for
       Dental Materials and Devices, Secretariat, Council
       on Dental Materials and Devices, American Dental
       Association (see reference 9 for address).

97.   Hedegård, B. Cold-polymerizing resins, a clinical
       and histological study. Acta. Odontol. Scand.
       13:13-126 Supplement 17, 1955.

98.   Brauer, G. M. EBA cements, 50th Anniversary
       Symposium on Dental Materials Research at the
       National Bureau of Standards . (To be published.
       Meanwhile, a copy may be obtained from the Dental
       Research Section, National Bureau of Standards,
       Washington, D. C. 20234.)

99.   Index to Dental Literature. A Cumulative Quarterly
       published by the American Dental Association, (see
       reference 9).

100.   Oral Research Abstracts, a monthly published by
       the American Dental Association (see reference 9).

101.   Guide to Dental Materials and Devices, published

        biennially by the American Dental Association.

        (see reference 9).

102.   Bibliography of Publications by the Dental Research

        Section of the National Bureau of Standards,

        Washington, D. C. 20234.   (May be obtained upon

        application.)

103.   Skinner, E. W. and Phillips, Ralph W.   The Science

        of Dental Materials, W. B. Saunders Co., Philadelphia,

        Pa. 1967.

104.   Peyton, et al. Restorative Dental Materials, The

        C. V. Mosby Co., St. Louis, Mo. 1968, 3rd Ed.

105.   Anderson, J. M. Applied Dental Materials.

        Blackwell Scientific Publications, Oxford, England,

        1967.

106.   Journal of Dental Research, the bimonthly Journal

        of the International Association for Dental Research

        (see reference 28 for address).

107.   Phillips, R. W. and Ryge, G. Adhesive Restorative

        Dental Materials. (Proceedings from a workshop

        sponsored by the Dental Study Section, National

        Institutes of Health and supported by a grant

from the National Institute of Dental Research.)
Owen Litho Service, Spencer, Indiana. Published
1961.

108. Adhesive Restorative Materials II. (Proceedings
from the second workshop sponsored by the Bio-
materials Research Advisory Committee, National
Institute of Dental Research.) Public Health
Service Publication No. 1494 (1966). For sale
by the Supt. of Documents, U. S. Government
Printing Office, Washington, D. C. 20402.
Price $1.00.

109. National Institute of Dental Research, Research
Contracts Office, Room 403 Westwood Building,
Bethesda, Md. 20014 will furnish a list of Clearing-
house Numbers of the Reports of Research Contractors
with N.I.D.R. Copies of these reports may be obtained
from the   National Technical Information Service,
                        Springfield, Va. 22151.

110. Science Information Exchange, Smithsonian Institution,
300 Madison National Bank Building, 1730 M Street
N. W., Washington, D. C. 20036. This is a National
Registry of Research in Progress where retrieval
service for queries is available.

111.   Gilmore, H. W. Text book of operative dentistry.
       The C. V. Mosby Co., St. Louis, Mo. 1967.

112.   Schultz, L. G. et al. Operative dentistry. Lea
       & Febiger, Philadelphia, Pa. 1966.